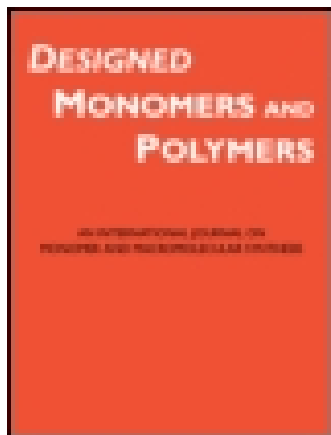


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Synthesis and characterization of novel ABA-type azobenzene-containing tri-block copolymers from telechelic polystyrene

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The telechelic polystyrene (tPS) was used as a macro-reversible addition fragmentation chain transfer (RAFT) agent to prepare the ABA-type tri-block copolymers (TBCs), poly{4-[4-(11-acryloyloxyundecyloxy)phenylazo]benzotrile}-*b*-polystyrene-*b*-poly{4-[4-(11-acryloyloxyundecyloxy)phenylazo]benzotrile} [poly(AUPAB)-*b*-PS-*b*-poly(AUPAB)] with 4-[4-(11-acryloyloxyundecyloxy)phenylazo]benzotrile (AUPAB) as a monomer by the RAFT polymerization process. The poly(AUPAB) was used as a reference to probe the role of polystyrene block in poly(AUPAB)-*b*-PS-*b*-poly(AUPAB) macromolecular chain. The TBCs were characterized by spectral techniques, thermal analysis, and polarizing optical microscopic studies and compared the results with individual blocks, poly(AUPAB), and tPS. The TBCs exhibited higher thermal stability and liquid crystal–isotropic phase transition peak temperature (T_{LC-I}), and glass transition temperature (T_g) values compared to the poly(AUPAB). TBC T_{LC-I} value was dependent on the AUPAB wt% in macromolecular chain. Furthermore, the acquired results by optical microscopy suggest that after incorporation of the polystyrene block in acrylate-based pendant azobenzene polymer chain resulted in lower domain size of focal conic texture, which is characteristic of smectic-A liquid crystalline phase compared to the homopolymer. The photophysical properties of the TBCs were similar to those of the poly(AUPAB). Microphase-separated nano-segregation was observed in annealed thin films of TBCs.

Keywords: styrene-based telechelic macro-RAFT agent; azobenzene polymers; ABA-type tri-block copolymers; RAFT process; liquid crystalline polymer

Introduction

Design and synthesis of azobenzene [1]-containing macromolecular architecture is one of the major current research areas. These materials resulted in reliable reversible photoisomerization, photoalignment, and photoinduced cooperative motion for various applications such as actuators, holographic,[2,3] and a photoswitchable responders.[4–9] Pendant azobenzene groups in side-chain liquid crystalline (LC) polymers influence the material properties such as in light-driven two-dimensional movement and bending of LC elastomers and assist microphase separation to obtain well-ordered nanostructure assemblies in block copolymers. It has also been reported that the variation in volume fraction and azobenzene location [10,11] in macromolecular architecture [12–14] can tune the material crystallization, optical transparency, LC elastomeric nature, and photoinduced electro-optical properties.

In general, azobenzene polymers were obtained by the direct polymerization of azobenzene-containing monomers and post-functionalization [15,16] of pre-polymers. At the initial stage of the development, pendant azobenzene polymers had been synthesized mainly by classical free radical polymerization (FRP) of azobenzene pendant

(meth)acrylate monomers. These homopolymers [17–20] and copolymers [21] were used to demonstrate their multi-responsive reversible gel character, supramolecular photomechanical systems,[22] optical switching, and image storage applications.[23] Classical FRP is not talented to control the polymer molecular weights and targeted architecture of the macromolecular chains, which are solely responsible for the polymer physical properties. Therefore, it is necessary to control the macromolecular architecture by adopting controlled polymerization methods, such as ionic and controlled FRP methods. A number of researchers synthesized polystyrene or poly(methyl methacrylate) block possessing AB type azobenzene LC copolymers using anionic polymerization [24] in controlled manner in quantitative yields with narrow molar mass distribution.[25,26] Recently, well-defined and controlled architecture of the azobenzene-containing polymers were successfully synthesized using straightforward controlled FRP methods. In the past, side-chain azobenzene methacrylate di-block and ABA type tri-block copolymers (TBCs) were synthesized using atom transfer radical polymerization (ATRP) method.[27–30] On the other hand, the RAFT process competes with classical FRP to the concerned of maintaining narrow polydispersity and

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living nature. Using the RAFT process, the azobenzene-containing homopolymers,[31–33] di-block copolymers, [34–36] Ag nanoparticles at the terminal end [37] of the polymer chain, push and pull structures [38] of the azo pendants, and tetrazole-containing [39] azo polymers were successfully prepared for photoinduced birefringence and surface-relief-gratings applications. However, before the discovery of the ATRP and RAFT, Otsu et al. reported that the tetraethylthiuram disulfide was able to polymerize styrene by thermally (*iniferter* process) to produce tPS and it was further photoinitiated to construct ABA type copolymers in living nature.[40–42] By following the similar procedures, photoinitiated ABA type LC block copolymers [43] and fluorinated AB and ABA type copolymers [44,45] were reported. This method suffers lack of molecular weight control and not amenable to a wide variety of functional monomers. In particular, it failed to polymerize photolabile group containing monomers. We herewith report for the first time the initiation of tPS (B block) by radical initiator to produce ABA type TBCs having acrylate-containing pendant azobenzene segments (A block), and characteristics of the resulted block polymers were compared with acrylate containing pendant azobenzene homopolymer to understand the polystyrene block role in TBC.

Experimental

Materials

4-Aminobenzonitrile, triethylamine and azobisisobutyronitrile (AIBN) (Avra); acryloyl chloride (Hychem); 2-cyano-2-propyl dodecyltrithiocarbonate (CPDTC); 11-bromoundecanol and tetraethylthiuram disulfide (Sigma-Aldrich); anisole, ethanol, and methanol (Finar Chemicals Ltd); dry 1,4-dioxane (Spectrochem); tetrahydrofuran (THF); toluene and hydrochloric acid (Rankem); phenol, sodiumhydroxide (NaOH), sodiumnitrite, and molecular sieves 4 Å (sd fine-chem Ltd) were used as received. Styrene (Avra) was purified by washing with aqueous NaOH and water and dried over sodium sulfate (sd fine-chem Ltd) at cold condition. Afterward, it was distilled at 40 °C under reduced pressure prior to use. Anisole (Sisco Research Laboratories Pvt. Ltd) was dried by refluxing over sodium metal up to 2 h and distilled before prior to use. THF was dried over sodium metal and benzophenone.

Polymerization

Polymerization of the 4-[4-(11-acryloyloxyundecyloxy)-phenylazo]benzonitrile (AUPAB)

The monomer, AUPAB, was synthesized according to the reported procedure.[27] The AUPAB was polymerized

via RAFT method.[46] A mixture of AUPAB (1 g, 2.24 mmol), AIBN (9.8 mg, 0.06 mmol) and RAFT agent, CPDTC (31 mg, 0.09 mmol) in 10 mL of dry THF, was deoxygenated by three times of freeze–pump–thaw cycles. Then, the flask was sealed and heated to 80 °C under stirring and allowed this condition for 30 h. After the period, the polymerization was terminated by the addition of 0.5 mL of methanol and exposing to air. The poly(AUPAB) was isolated by threefold of precipitation in cold methanol. Yield: 20%.

Preparation of tPS

Tetraethylthiuram disulfide (4 g) and 60 mL of styrene were dissolved in 60 mL of THF in a 500-mL round-bottom flask [43,44], and the mixture was deoxygenated three times by freeze–pump–thaw cycles, and the flask was sealed and kept at 75 °C oil bath with constant stirring. After 5 h, the polymer was recovered by THF evaporation on rota evaporator at room temperature. The viscous mixture was precipitated in excess amount of methanol. The precipitate was purified twice by dissolving in THF and re-precipitating in methanol. Yield: ~20%. FTIR (KBr, Cm^{-1}): ν 1415 ($-\text{N}-\text{C}=\text{S}$),[47] ν 1024 ($-\text{C}=\text{S}$), and ν 541 ($\text{C}-\text{S}$). ^1H NMR (300 MHz, CDCl_3): δ 6.30–7.26 (Ar-H), δ 3.60 and 4.00 ($-\text{N}-\text{CH}_2-$), δ 1.66–2.18 ($-\text{CH}-$, back bone), δ 1.26–1.66 ($-\text{CH}_2-$, back bone), and δ 1.08–1.26 ($-\text{CH}_3$, terminal ends). ^{13}C NMR (125 MHz, CDCl_3): δ 145.1, 127.9, 125.6, 39.8–49.7, and 11.6. In UV–vis spectrum, λ_{max} was at 282 nm (0.133 abs) due to *N,N*-diethyldithiocarbamate end groups and 253 nm (0.192 abs) due to combination of phenyl rings of the polystyrene back bone and the dithiocarbamate end groups in THF (2 mg in 25 mL). The tPS calculated molecular weight from ^1H NMR was 2973, by considering 2 end terminal groups per one macromolecular chain (ideal conditions, chain terminal end groups functionality is 2). By size exclusive chromatography (SEC) data, the tPS number average molecular weight (M_n) was 2634 and dispersity (M_w/M_n) was 1.75. The macromolecular chain terminal end groups functionality was calculated with ^1H NMR spectrum and SEC data of tPS. At first, the number of repeating units (24) of the tPS macromolecular chain was calculated from SEC data. Then, the phenyl rings signals intensity (24×5) was taken as 24 repeating units in ^1H NMR spectrum, and with that relative value, the terminal ends were calculated. It was 1.75. In addition to that, the chain terminal end groups presence was confirmed by thermogravimetry (TG) curve. The TG curve showed two stage of degradation, first-stage degradation [48] (120–265 °C) was corresponding to terminal end groups degradation, where weight loss was about 6.01 wt% which was matching with the value of calculated terminal end groups of the macromolecular chain

(5.47 wt%) [(macromolecular chain terminal end groups molecular weight $\div M_n$) $\times 100$].

Preparation of poly{4-[4-(11-acryloyloxyundecyloxy)phenylazo]benzotrile}-b-polystyrene-b-poly{4-[4-(11-acryloyloxyundecyloxy)phenylazo]benzotrile} [poly(AUPAB)-b-PS-b-poly(AUPAB)] TBCs

Typical polymerization procedure was as follows. A mixture of AUPAB (750 mg, 1.68 mmol), AIBN (8.2 mg, 0.05 mmol) and macro-RAFT agent, tPS (132 mg, 0.05 mmol) in 8 mL of dry anisole/2.5 mL dry 1,4-dioxane was deoxygenated by three times of freeze-pump-thaw cycles. Subsequently, the flask was sealed and heated to 80 °C under stirring and allowed this condition for 20 h. Then, the polymerization was terminated by the addition of 0.5 mL of methanol and exposed to air. The polymer was isolated by twofold precipitation in cold methanol and one time in ethylacetate and *n*-hexane (15:85 v/v) mixture. Yield: 40%.

Thin film preparation

The homopolymer or TBC (5 mg mL⁻¹) was dissolved in 1:4 (v/v) ratio of the THF and toluene mixture. A few drops of the polymer solution were added using a chemical dropper on quartz plate, which was placed on the base of spin coater (APEX Instruments Co. SCU 2005) and allowed 30 s at room temperature, followed by 750, 1250, and 750 rpm rotation with each stage for 30 s. These spin-coated films were kept under dark conditions for 6 h before measuring the UV-vis absorption spectra. After measuring the spectra, the films were annealed at 113 and 140 °C for TBC-1 and TBC-2, respectively, for 15 h under vacuum condition and measured UV-vis absorption spectra.

Measurements

The FTIR spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer at a resolution of 4 cm⁻¹ using KBr optics at room temperature, and a minimum of 32 scans were signal averaged. The NMR spectra were recorded on AVANCE or INOVA spectrometer in CDCl₃/DMSO-d₆ with tetramethylsilane as an internal standard, and the magnetic field frequencies were 300 or 500 MHz for ¹H NMR and 60 or 125 MHz for ¹³C NMR measurements. Mass spectra (ESI-MS) were recorded on FINNIGAN LCQ Advance Max in methanol. The absorption spectra were recorded on Spectro UV-vis double beam PC, 8-scanning auto cell, LABOMED INC. Melting points of the small molecules were obtained on apparatus VEEGO, model: VMP-D. The SEC was performed using a Shimadzu system built in with one (300 \times 7.5 mm) PLgel 5 μ m 10E3Å column (VARIAN) and evaporative light-scattering

(PL-ELS), and refractive index detectors (Polymer Laboratories). The eluent was THF (HPLC grade) and a flow rate of 0.5 mL min⁻¹ at 30 °C. Calibration for detector response was gained using single narrow polystyrene standards (molecular weights: 1480; 3950; 10,680; and 31,420 from Polymer Labs). One milligram of polymer was dissolved in 1 mL of THF. Values of M_n and M_w/M_n were determined using LC Solution for Windows software. The TG curves were obtained from TGA Q500 thermal analyzer at heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Thermal analyses were performed by a differential scanning calorimeter, DSC Q100 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Typical procedure was as follows. The sample was first equilibrated to -70 °C and heated (first heating) from -70 to 170 °C at 10 °C min⁻¹, and then, it was cooled (first cooling) from 170 to -70 °C at a rate of 10 °C min⁻¹ using TA, Refrigerated Cooling System 90. Then, the sample was again heated (second heating) from -70 to 170 °C at a rate of 10 °C min⁻¹, and then, it was cooled (second cooling) from 170 to -70 °C at a rate of 10 °C min⁻¹. The second heating and cooling curves were reported. The LC behavior of the polymers was examined by polarizing optical microscopy (POM) (Nikon, POL100 V) using a heating stage and temperature controller (Mettler FP 90). XRD measurement was made on non-oriented polymer sample. The polymer was filled into a Lindemann capillary tube of diameter 0.5 mm in the isotropic phase, and the ends were flamed sealed. The diffraction pattern was recorded on an image plate while cooling. Wide-angle X-ray diffraction (XRD) profiles of the polymers were recorded using a Bruker D-8 Advance power XRD instrument (anode: Cu - WL1: 1.5406), from 2 to 65° at a step of 0.013° and step time of 13.6 s at room temperature. The TEM (JEOL, 200KV, Japan.) images of thin films on TEM grids were recorded. The samples were prepared as following procedure. 0.5 wt% polymer solution (in 1:4 THF and Toluene) was poured onto water surface and then transferred the obtained thin films onto TEM copper grids. These grids were annealed for 72 h at 113 and 140 °C for TBC-1 and TBC-2, respectively. Then, a droplet of uranyl acetate (2 wt %) in ethanol was deposited onto the annealed films. After 1 min, the excess solution was removed by a piece of filter paper by capillary action.

Results and discussion

The poly(AUPAB)-b-PS-b-poly(AUPAB) TBCs were synthesized by RAFT process using AIBN as an initiator, tPS as a macro-RAFT agent, and the AUPAB as a monomer. As a reference, the homopolymer of the AUPAB was polymerized by RAFT process using the CPDTC as a RAFT agent. The chemical structures of the polymers are shown in Scheme 1. The synthesized homopolymer (HP) and TBCs with 43 (TBC-1) and

87 wt% (TBC-2) of azobenzene content in copolymer showed monomodal SEC curves, and the molar masses are summarized in Table 1. The molecular weights of the HP and TBCs were calculated from ^1H NMR spectra using Equations (1) and (2).

$$\text{HP molecular weight} = \text{AUPAB}(f_w) \times [(I_{4.03} \div I_{3.32}) \div 2] + \text{CPDTC}(f_w) \quad (1)$$

where AUPAB(f_w): AUPAB monomer molecular weight, $I_{4.03}$ and $I_{3.32}$: intensities in ^1H NMR spectra at δ 4.03 and 3.32 ppm, and CPDTC(f_w): RAFT agent molecular weight.

$$\begin{aligned} \text{TBC molecular weight} &= \text{tPS}(M_{\text{NMR}}) + \text{AUPAB}(f_w) \\ &\times [(I_{\text{azo}}I_{7.68-8.02} \div 6) \\ &\div (\text{tPS}I_{6.28-6.78} \div 54)] \end{aligned} \quad (2)$$

where tPS(M_{NMR}): molecular weight of tPS from ^1H NMR, I_{azo} and $I_{7.68-8.02}$: intensities in ^1H NMR spectra for azo block at δ 7.68–8.02 ppm and for tPS block δ 6.28–6.78 ppm.

The calculated molecular weights from the ^1H NMR spectra and SEC values of the HP and TBC-1 had good agreement with each other, whereas the TBC-2 molecular weight was conflicted with the SEC value. A similar observation was made for azobenzene block copolymers by Zhao et al.[35] The FTIR spectra of the HP and TBCs showed characteristic bands around 2227, 1733, and 1468 cm^{-1} due to the stretchings of cyano, ester carbonyl, and azobenzene groups, respectively. The ester carbonyl stretchings of the HP and TBCs were shifted about 14 cm^{-1} higher wavenumber compared to the monomer ester carbonyl. The HP and TBCs were readily soluble in polar aprotic solvents such as dimethylformamide, dimethylacetamide, *N*-methyl-2-pyrrolidone and

THF and in chlorinated solvents, for instance, chloroform, 1,2-dichloroethane and dichloromethane.

The ^1H NMR spectrum of the TBC-1 (Figure 1(a)) showed broad and coalesced signals centered at δ 7.90, 7.76, and 6.97 ppm due to the azo block benzene protons, and δ 7.10 and 6.59 ppm signals were due to the benzene protons of polystyrene block. The TBC signals of the $-\text{O}-\text{CH}_2-$ methylene (centered at δ 4.05 ppm), pendant methylene spacer, polymer backbone methylene and methine protons, and terminal ends of the polymer chain (δ 0.8–2.7 ppm) were observed similar to the homopolymer. The signals at δ 3.2–3.7 ppm indicated the living nature of the macromolecular chain terminal ends ($-\text{N}-\text{CH}_2-$) of the TBC-1. In the case of TBC of higher molecular weight, from M_w : 12,385 onwards, the terminal end $-\text{N}-\text{CH}_2-$ signals were not observed in ^1H NMR spectrum. It indicates that the living nature of the macromolecular chain disappeared. The ^{13}C NMR signals of the TBC were in good agreement with the assigned macromolecular structure as shown in Figure 1(b).

The HP and TBCs had three stages of thermal degradation, whereas tPS exhibited two-stage degradation under nitrogen atmosphere as shown in Figure 2. The TBCs onset decomposition temperatures were higher about 40 $^\circ\text{C}$ compared to the HP. The temperatures of 5% (T_{d5}) and 10% (T_{d10}) weight loss of the HP, tPS, and TBCs are presented in Table 2. The T_{d5} and T_{d10} values of TBCs were higher compared to the HP. Hence, we deduce that this could be due to the incorporation of polystyrene block in the middle of the acrylate-based azobenzene polymer chain. Higher molecular weight TBC-2 exhibited about 8 $^\circ\text{C}$ higher thermal stability at T_{d5} compared to their respective low molecular counterpart (TBC-1). This is due to the vanishing of chain terminal end functional groups for higher molecular weight TBC-2 in the process of the polymerization. We observed that the chain terminal end $-\text{N}-\text{CH}_2-$ signals were not noticed in ^1H NMR spectrum for the TBC-2.

Table 1. RAFT polymerization experimental conditions.^a

Polymer code	Solvent	[AUPAB] ₀ ^b	[RAFT agent] ₀ ^b × 10 ²	Molecular weight (^1H NMR)	SEC		AUPAB content ^c /wt%
					M_w g mol ⁻¹	M_w/M_n	
<i>Homopolymer</i>							
HP	THF	0.22	0.89	5497 ^d	5089	1.26	94.07
<i>Tri-block copolymer</i>							
TBC-1	Anisole	0.21	0.63	5178 ^e	6699	1.60	43
TBC-2	Dioxane	0.67	2.01	23311 ^e	13,394	1.32	87

^a[AUPAB]:[CPDTC]:[AIBN] = 75:3:2 (HP), [AUPAB]:[tPS]:[AIBN] = 100:3:3 (TBC-1 and 2), polymerization temperature: 80 $^\circ\text{C}$, and time: 30 h.

^bIn feed.

^cCalculated from ^1H NMR spectrum.

^dObtained from Equation (1).

^eObtained from Equation (2).

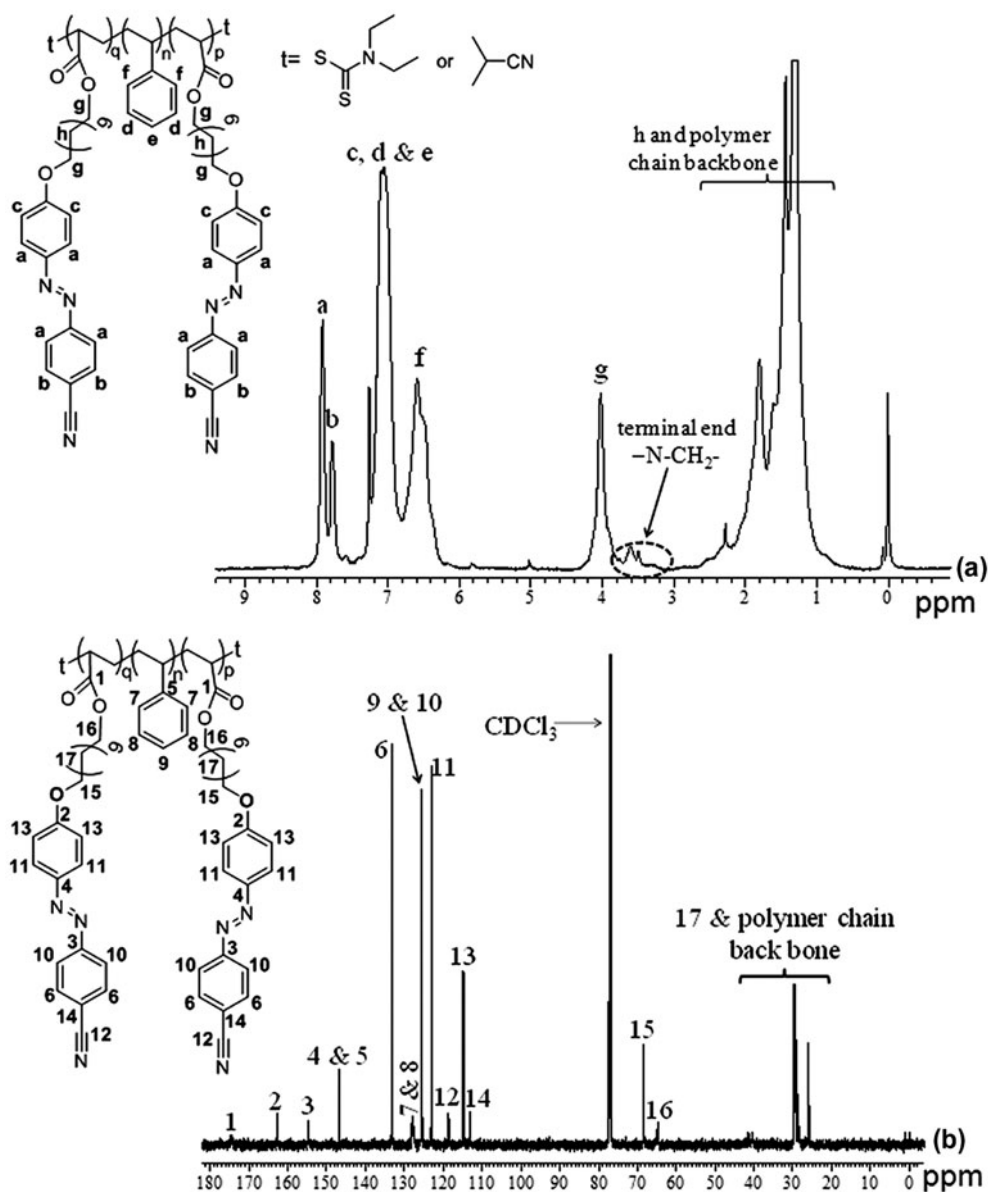


Figure 1. NMR spectra of poly(AUPAB)-*b*-PS-*b*-poly(AUPAB) of (a) ^1H and (b) ^{13}C .

The DSC thermogram of the HP exhibited T_g value at 17 °C, and an endothermic peak centered at 100 °C, which is assigned to a LC-isotropic phase transition temperature ($T_{\text{LC-I}}$) on heating cycle, and the crystal transition temperature (T_c) was at 98 °C as shown in Figure 3. In the case of the TBC-1 with 43 wt% pendant azobenzene content, the thermogram revealed two T_g points. The first T_g was assigned to segmental mobility of poly (AUPAB) blocks, at about 29 °C, and the second T_g was due to the polystyrene block, at about 85 °C, while the neat tPS showed T_g at 81 °C. This indicates that the TBC-1 exhibited phase separation [43,49,50] behavior. On the other hand, having 87 wt% of azobenzene content, TBC-2 exhibited single T_g point at 30 °C. The

$T_{\text{LC-I}}$ in the TBCs increased with increasing the pendant azobenzene content (121 °C for 43 wt% azobenzene content (TBC-1) and 148 °C for 87 wt% azobenzene content (TBC-2)) as shown in Table 2. The increase in T_g and $T_{\text{LC-I}}$ values of the TBC compared to the HP may be due to the differences in polymer chain terminal end groups and azobenzene aggregations by phase separation [35] causes the changes in crystal packing of the macromolecular chains.

The HP and TBCs LC behaviors were examined, and the representative polarized optical micrographs are shown in Figure 4. A typical focal conic texture, characteristic of smectic-A (SmA) phase was observed in both heating and cooling cycles of the polymers.

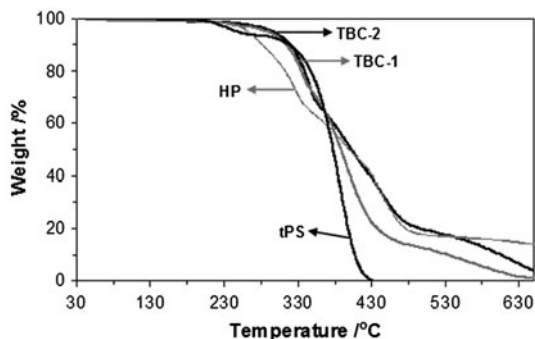


Figure 2. TG curves of synthesized homopolymer, tPS, and TBCs.

The incorporation of polystyrene block in acrylate-based pendant azobenzene polymer chain exhibited SmA liquid crystal phase with lower focal conic domain size compared to the homopolymer.[43] The XRD pattern of TBC (TBC-2) at 115 °C is shown in Figure 5. In the small angle region, it showed only one small peak corresponding to a d spacing of 21.1 Å ($2\theta = 4.1^\circ$) and a broad diffuse wide-angle reflection at about 4.1 Å ($2\theta = 21^\circ$) indicating a liquid-like in-plane order. As this is a side-chain liquid crystalline polymer and exhibited a smectic type texture, at the very small angle, that is $2\theta < 4.1^\circ$, a sharp peak corresponding to spacing of about 42.2 Å is expected, which was beyond the layer accessible range of our instrument. The ratio of expected and observed ($2\theta = 4.1^\circ$) layer spacing is 1: $\frac{1}{2}$. The approximate calculated length of the side-chain of the macromolecule (considering the bond length) is about 38 Å, which is closer to the expected value (42.2 Å). As both the values are comparable, we conjecture that this is the first-order signal of a SmA₁ mesophase. Isotropic phase transition temperatures (T_{iso}) of the HP (T_{iso} : 140 °C), TBC-1 (T_{iso} : 150 °C), and TBC-2 (T_{iso} : 168 °C) were observed using optical polarized microscope on heating. The polarized optical micrographs of the polymers around T_{iso} are given in supporting information.

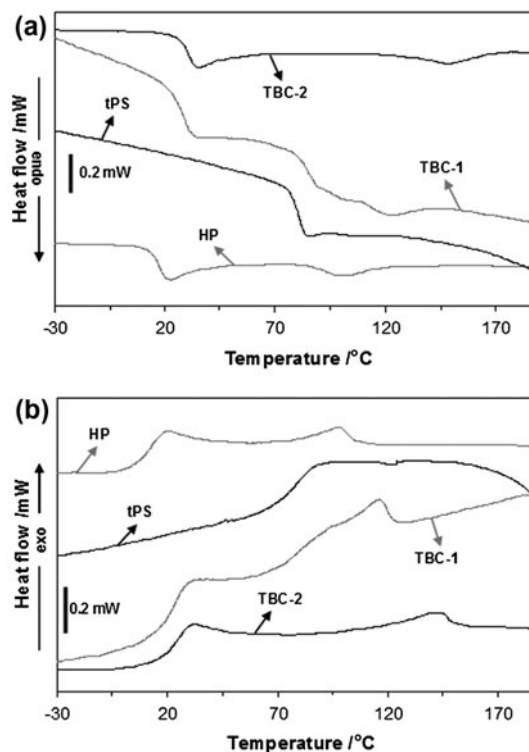


Figure 3. DSC curves of homopolymer, tPS, and TBCs (a) heating and (b) cooling cycles.

The HP and TBCs exhibited λ_{max} at about 365 nm due to $\pi-\pi^*$ and 436 nm due to $n-\pi^*$ electronic transitions in THF solution (0.5 mg/25 mL) (Figure 6(a)). The spin-coated HP and TBC-2 films exhibited λ_{max} at about 335 nm corresponding to H-type aggregation [51,52] and along with a sudden jump in absorbance (more or less in all spectra) toward higher wavelengths, at 360 nm (Figure 6(b) and (c)) corresponding to likely related with the lamp change in instrument and combined with the non-associated azobenzene groups present in the film. The HP and TBCs films spectra were broad in nature compared to the spectra obtained in THF solution.[51] After annealing the spin-coated films in LC phase, the

Table 2. Thermal characteristics of the synthesized polymers.

Polymer code	TGA ^a		DSC ^b		
	$T_{d5}/^\circ\text{C}$	$T_{d10}/^\circ\text{C}$	$T_g/^\circ\text{C}$	$T_{LC-I}/^\circ\text{C}$ ($\Delta H/J \text{ g}^{-1}$)	$T_c/^\circ\text{C}$ ($\Delta H/J \text{ g}^{-1}$)
HP	262	282	17	100 (4.48)	98 (5.56)
tPS	248	318	81	— ^d	—
TBC-1	289	314	29, 85	121 (1.17)	116 (1.67)
TBC-2	297	319	30	148 (4.1)	142 (6.0)

^aTemperatures of 5 and 10% weight of the sample decomposition.

^bObtained from DSC second heating curve.

^cEndotherm peak temperature.

^dNot observed.

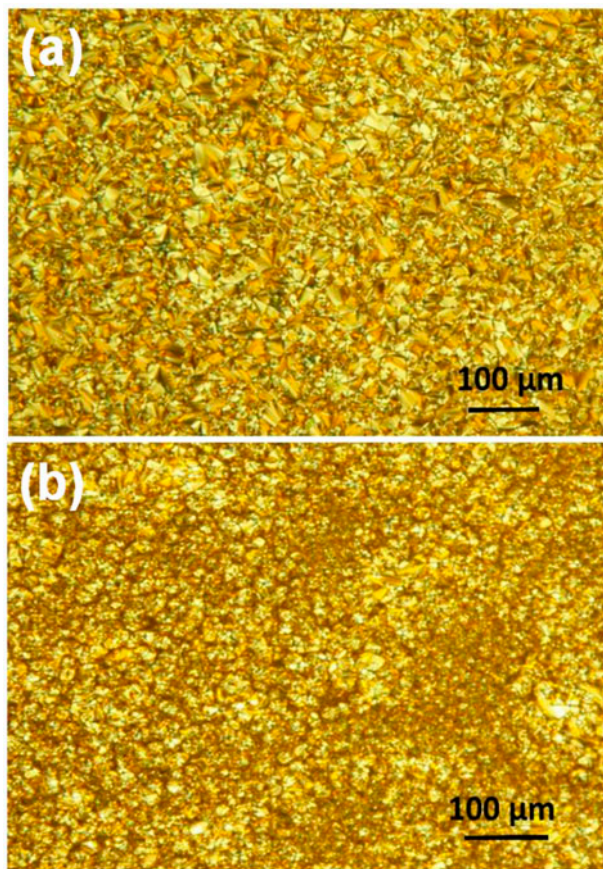


Figure 4. Photomicrograph of (a) HP and (b) TBC-2 at 60 °C.

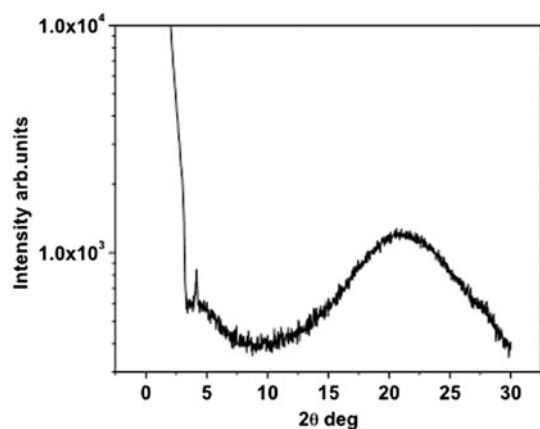


Figure 5. X-ray intensity as a function of angle 2θ of TBC-2 at 115 °C.

λ_{max} was shifted to about 32 nm higher wavelength and the absorbance decreased by about 65% for HP and TBCs.[53,54]

The pendant azobenzene group *E*-*Z* configurations were calculated with ambient light and conventional

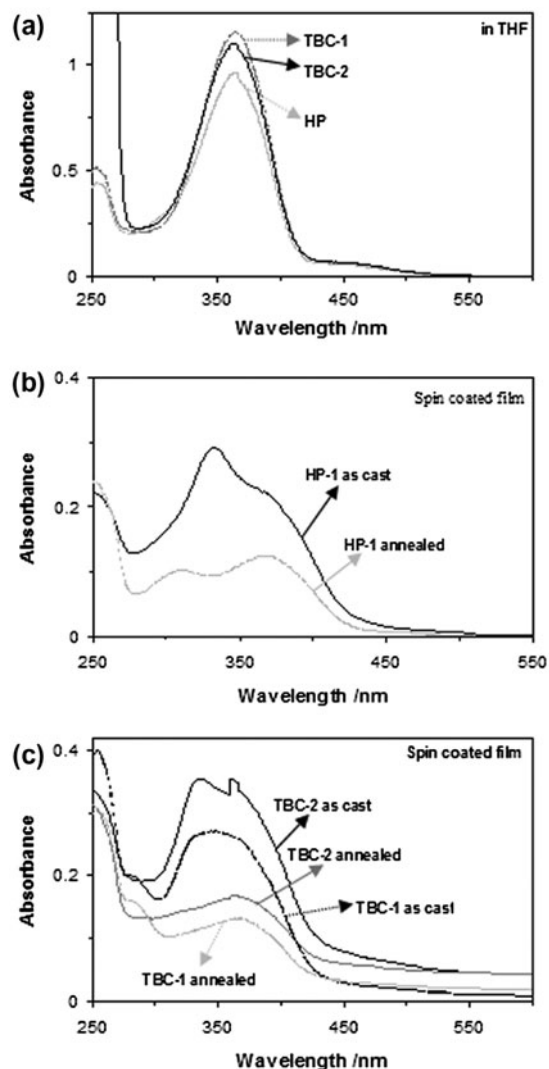


Figure 6. UV-vis absorption spectra of (a) poly(AUPAB) and poly(AUPAB)-*b*-PS-*b*-poly(AUPAB) in THF and as cast and annealed films of (b) poly(AUPAB) and (c) poly(AUPAB)-*b*-PS-*b*-poly(AUPAB) at room temperature.

fluorescent tube light exposure, while preparing the sample without UV irradiation at room temperature in CDCl₃ solution by ¹H NMR spectra. The monomer, AUPAB, *E*-configuration aromatic ring chemical shift values in ¹H NMR spectrum were centered at δ 7.93, 7.78, and 7.01 ppm, whereas *Z*-configuration showed the values in upfield,[34,55] such as, at δ 7.59, 6.92, and 6.75 ppm, respectively, as shown in Figure 7. A similar behavior was observed in the HP with broad signals, whereas the TBCs spectrum showed δ 7.59 ppm broad and overlapped signal with the *E*-configuration protons. The pendant azobenzene group *E*:*Z* ratios were 96:4 for monomer, 94:6 for HP, and 89:11 for TBC. The TBC higher *Z*-configuration value could be due to the overlapping of the *E*-configuration protons in ¹H NMR spectrum.

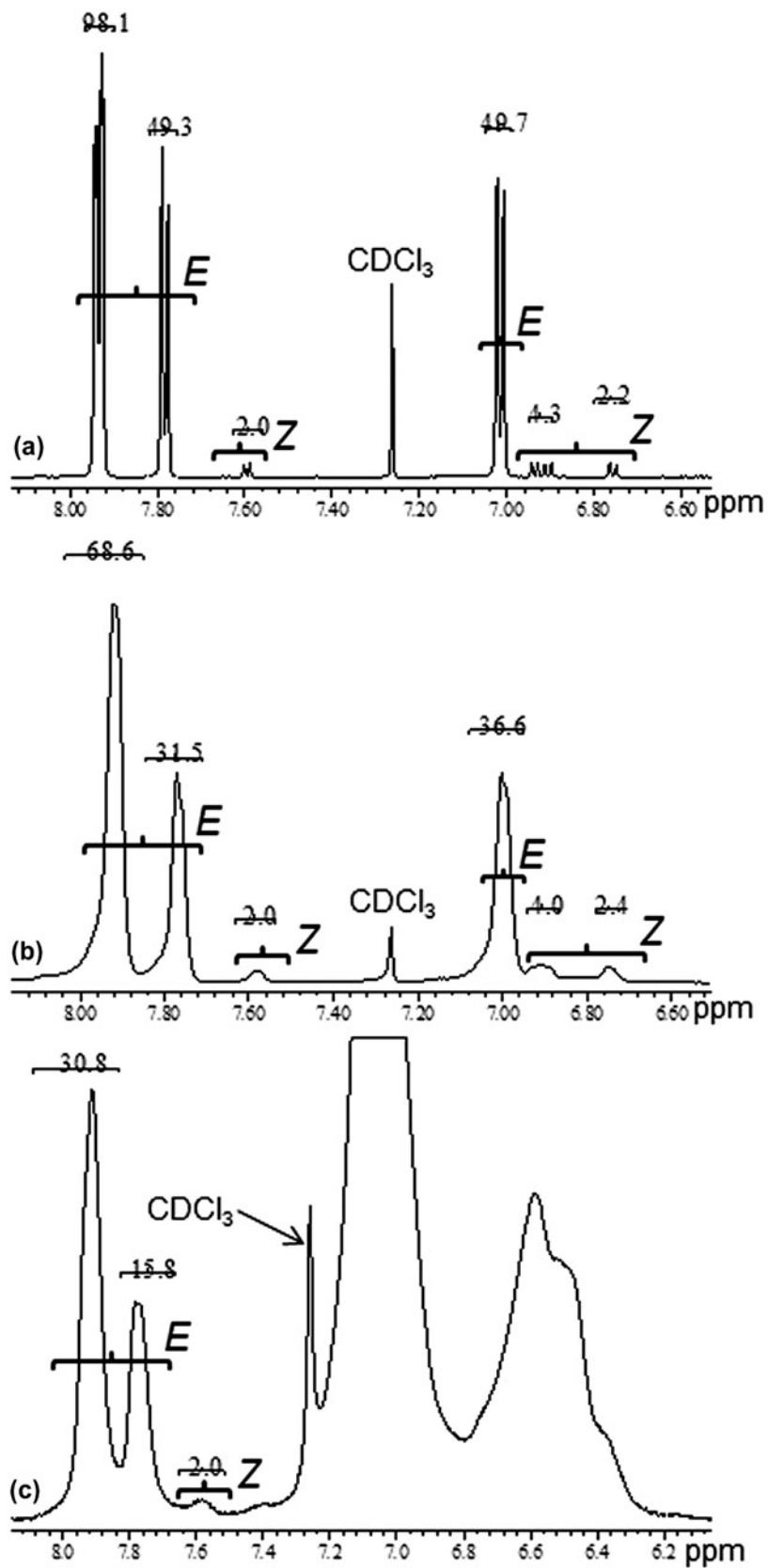


Figure 7. Magnified ^1H NMR spectra of (a) AUPAB, (b) poly(AUPAB), and (c) poly(AUPAB)-*b*-PS-*b*-poly(AUPAB) to calculate *E*- and *Z*-configurations ratio.

The spectra of spin-coated films (Spin NXG-p2) of the HP, TBC-1, and TBC-2 upon 365 nm UV light exposure (BLX-365, made in EEC, serial no: 0410512) with various radiation energies are shown in Figure 8. The HP and TBC-2 films exhibited the π - π^* absorbance decrease upon UV light exposure due to *trans/cis* isomerization until 128 mJ/cm² UV light energy, and then, π - π^* absorbance gradually increased upon increasing UV light energy up to establishing of photostationary state. The similar trend was observed by several research groups using annealed films.[27,56] In our case, in the spin-coated films, some extent of the azobenzene units were already in the upright orientation to the substrate plane, which were randomized upon UV light exposure and caused to increase in the π - π^* absorbance. On the other hand, the TBC-1 films exhibited slight and random changes in π - π^* absorbance intensities upon UV light exposure. This anomalous behavior may be due to the >50 wt% polystyrene content presence in the TBC,

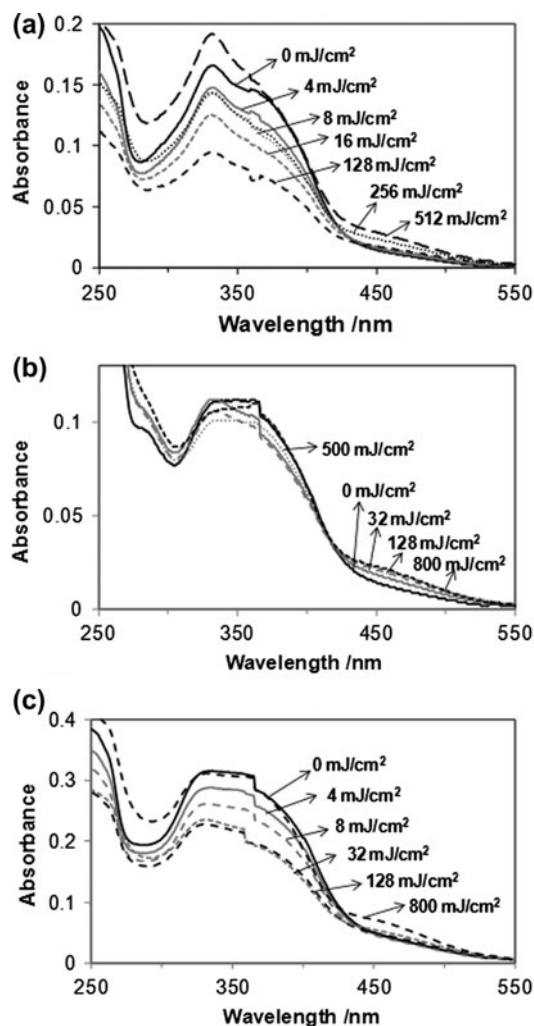


Figure 8. UV-visible absorption spectra of thin films of (a) HP, (b) TBC-1, and (c) TBC-2 upon exposure to 365 nm light.

which causes the geometrical restriction to azobenzene units for isomerization.

The features of the π - π^* absorbance at 331 nm spectral changes in the back process upon visible light irradiation (F8T5/BLB, Radium) by varying the exposure time for HP and TBC films after reaching photostationary state with 365 nm light are summarized in Figure 9. For the HP film, the absorbance increased with increasing irradiation time of 2 min and then decreased upon further irradiation and reached stable state. The earlier stage reflects the proceeding of *cis/trans* isomerization, and the following stages, decrease and reaching stable state, could indicate the contribution of upright orientation of the azobenzene units to the substrate plane.[56] The TBC-1 and TBC-2 films followed opposite trend to HP at initial stage (<2 min exposure). The magnitude of the absorbance decrease at initial stage was higher in TBC-2 compared to the TBC-1. This could be due to the contribution of more number of azobenzene units' upright orientation on the plane of measuring light direction upon light exposure, and further, light exposure azobenzene units achieved stable state.[57]

The nano-segregations were observed in TBC annealed thin films by TEM analyses, and typical TEM images of the TBC-1 and TBC-2 are presented in Figure 10. The TBC-1 exhibited LC azobenzene blocks as non-uniform spheres (relatively black regions) with a width/diameter about 30–92 nm dispersed into the PS matrix, whereas in TBC-2 thin films, PS block randomly aggregated as particles (relatively white regions) with a width/diameter about 2 nm dispersed into the LC azobenzene blocks matrix. It is also reported that a block copolymer with 85 wt% of LC fraction and 15 wt% of PS exhibited PS domains as dispersed segregations into bilayer LC matrix.[27,56,58] Phase separation behavior dependence with the volume ratio of PS and poly(AUPAB) blocks in TBC needs further investigation. Hence, we expect to use these macromolecular architectures design for developing nanotemplate applications in the future.

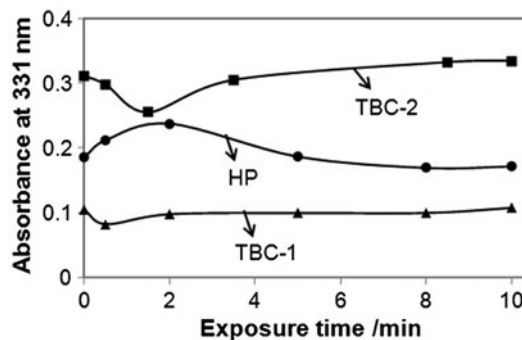


Figure 9. Changes in the absorbance at 332 nm in UV-visible spectra by varying visible light irradiation time for HP, TBC-1, and TBC-2.

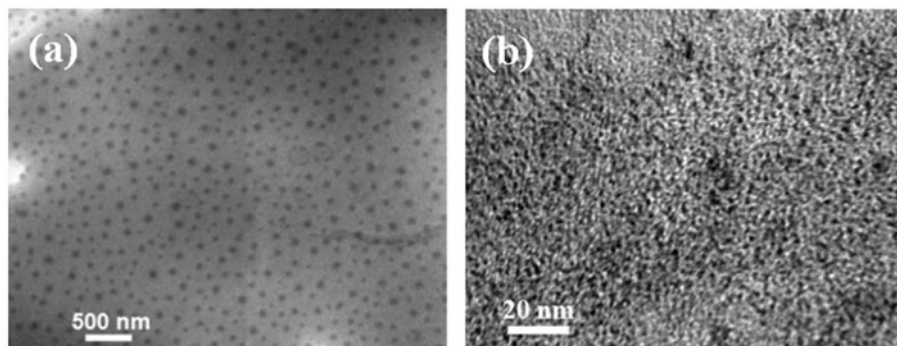
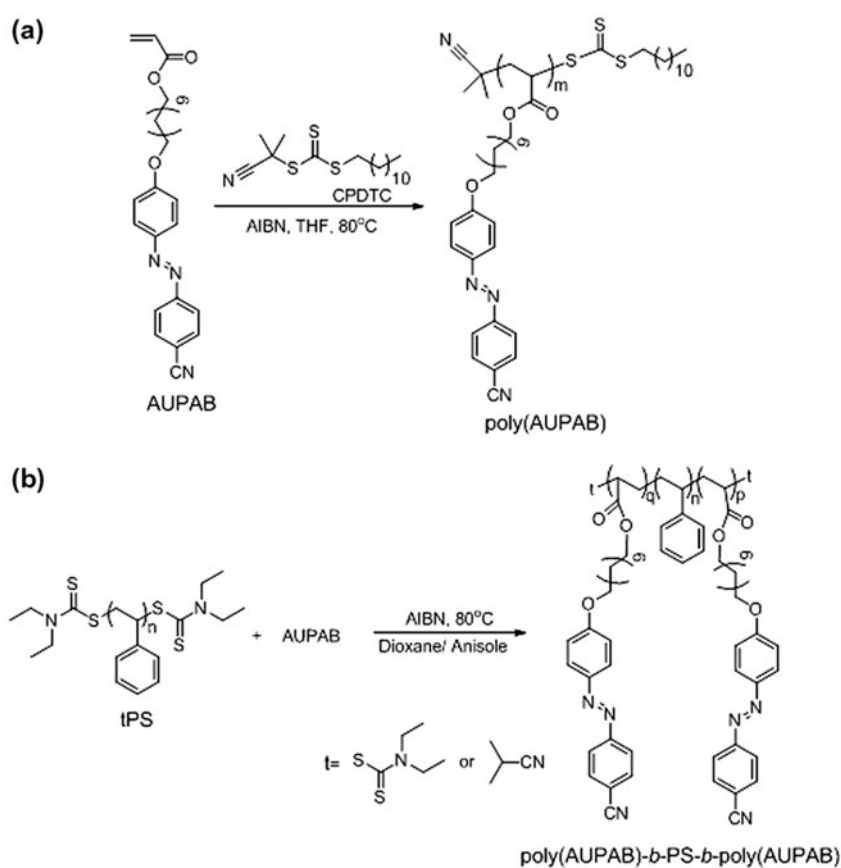


Figure 10. TEM images of TBC thin films of (a) TBC-1 and (b) TBC-2.



Scheme 1. Preparation of (a) homopolymer and (b) TBC by the RAFT process.

Conclusions

Azobenzene TBCs, poly(AUPAB)-*b*-PS-*b*-poly(AUPAB), composed of a central polystyrene block, and two lateral LC azobenzene polyacrylate blocks were for the first time successfully synthesized using telechelic polystyrene as a macro-RAFT agent by the reversible addition fragmentation chain transfer process. The synthesized TBCs exhibited higher thermal stability and higher T_g

and T_{LC-1} values compared to the homopolymer, poly(AUPAB). The TBC having 43 wt% azobenzene content showed phase separation by exhibiting two T_g values at 29 and 85 °C compared to the higher azobenzene content (87 wt%) TBC, which had single T_g value at 30 °C. The T_{LC-1} values of TBCs were dependent on the AUPAB wt % in the polymer chain. The incorporation of the polystyrene block in acrylate-based pendant azobenzene polymer chain showed smectic-A liquid crystalline phase

with lower focal conic domain size compared to the poly (AUPAB). The TBCs exhibited microphase-separated nano-segregation in thin films. Introducing polystyrene block into the LC polymer chain could render better film forming ability and expected as a potential material for coating applications.

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Supplementary data

Supplementary information for this article is accessed here <http://dx.doi.org/10.1080/15685551.2014.971396>.

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